ARMY RESEARCH LABORATORY

The Detection of Doped Cr Presence in $Sr_{0.6}Ba_{0.4}Nb_2O_3$ by SIMS

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Abstract

Photorefractive materials like SrBaNb (SBN) have optical properties that can have several military applications. To improve the figures of merit for these materials, it is very important to have better control of Cr dopant in the SBN. Since the amount of Cr dopant is so small, the usual analytical techniques are not adequate to analyze this material. In this report, the incorporation of Cr into SBN using secondary ion mass spectrometry (SIMS) measurement with an electron gun is confirmed.

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1. Introduction

Photorefractive (PR) materials are used for optical beam fanning, beam coupling, optical storage, and optical image processing [1]. These optical applications are critical for military purposes, such as protecting optical sensors. To maximize the protection capability, it is very important to increase the coupling coefficient and maintain a fast response time.

The control of the protection capability, i.e., the speed of response and coupling efficiency, requires a specific donor/acceptor ratio that is very difficult to realize using only a single dopant species. For this reason, the Rockwell Science Center introduced the double-doping concept and tried Cr^{3+}, which showed considerable promise in maintaining a fast response and a sufficiently high coupling coefficient.

SBN (Sr, Ba, Nb) crystals are grown along the (001) direction at the Rockwell Science Center using the Czochralski pulling technique from platinum crucibles in an oxygen atmosphere. To confirm the soundness of using Cr as a dopant, the Rockwell Science Center grew samples with different amounts of Cr dopant in the melts. In this study, we chose the materials doped with chromium only in the amounts of 0.005, 0.010, and 0.025 wt.% in the melts. The size of the samples was $6 \times 6 \times 6$ mm [2].

Analyzing these materials poses a challenge because the dopant concentration is too low for XPS/AES (x-ray photoelectron spectroscopy)/(auger electron spectroscopy), EDX/WDX (energy dispersive x-ray)/(wavelength dispersive x-ray) analytical techniques and because sample preparation for the AAS (atomic absorption spectroscopy) technique is very difficult. Therefore, we used the SIMS (secondary ion mass spectrometry) technique to prove the presence of Cr as a dopant as well as the amount by weight percent of Cr dopants. SIMS is the one of the most powerful techniques for the surface and depth profile analysis of materials.

SIMS typically provides detection limits between 1 ppm (part per million) and 1 ppb (part per billion), depending on instrumental transmission efficiency, detector efficiency, mass resolution, primary beam density, and matrix-related effects. SIMS instrumentation also provides a dynamic range of about nine orders of magnitude for secondary ion signal intensities.

This report details the dopant analyses conducted at the Army Research Laboratory of these photorefractive samples grown by the Rockwell Science Center.

2. Experiment

2.1 Equipment

The SIMS technique is widely used to investigate trace-level impurities and dopant distributions throughout the sample and to provide interface analysis for device fabrication. Many different kinds of SIMS exist, depending on the primary source and mass spectrometer, and pros and cons exist for each different type of SIMS instrument.

In this analysis, we used an ATOMIKA Ionprobe A-DIDA 3000 SIMS instrument with a quadruple mass filter as a mass analyzer for the secondary ions (see fig. 1). The primary source is the magnetically confined hot cathode oscillating electron bombardment type. We extracted positive argon gas from the discharge using a two-level electrostatic immersion system and accelerated the primary ion beam to energies between 1 and 15 keV. In addition to this, the machine is equipped with cold cathode mode, which can produce O_2^+ ions as well. The source lens arrangement was designed as a telefocus system, providing a beam spot with current densities continuously variable between 10^{-10} and 10^{-4} A/cm^2 and with good homogeneity across a 5-mm-diam sample spot at a distance of about 55 cm from the source exit hole. We used a unipotential lens to focus the space-charge-broadened telefocus beam into a 100-μm spot at the target surface. Two pairs of perpendicular deflection plates on the downstream side of the unipotential lens were used for beam scanning. Raster scanning of the primary beam, in conjunction with an electronic aperture, was used to reduce edge effects in depth profiling [3].

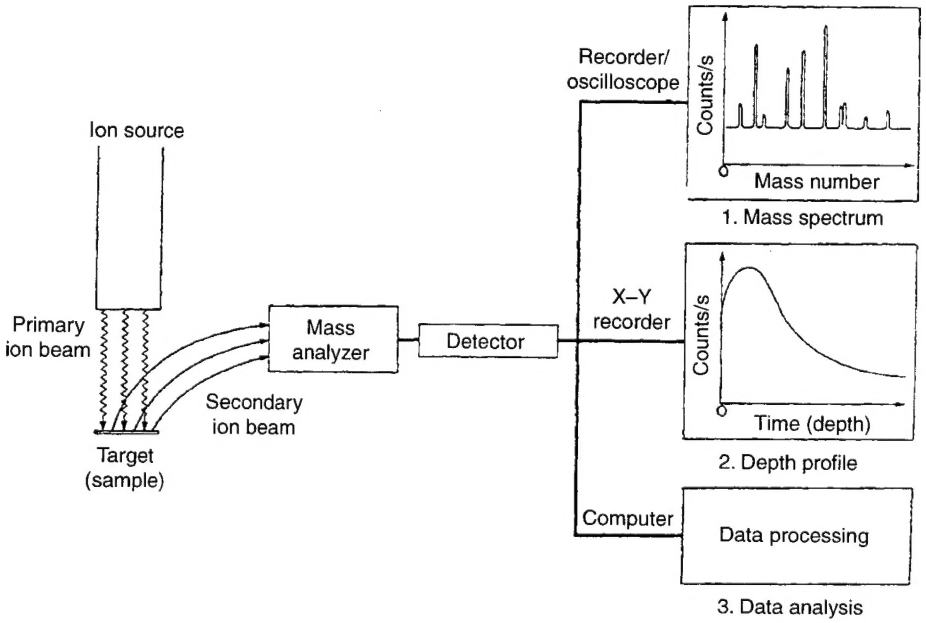

Figure 1. Secondary ion mass spectrometry (SIMS).

Proper selection of a narrow energy band pass for the secondary ions is essential for achieving good mass resolution in the quadruple mass spectrometer. In the ATOMIKA SIMS instrument, this energy selection is performed in a modified parallel-plate condenser. Some of the secondary ions emitted from the sample enter the condenser through an entrance diaphragm mounted off-axis with respect to the condenser centerline and the quadruple axis.

During SIMS analysis of samples with electrically insulating materials, a local charge builds up when samples are bombarded with a primary ion beam. This charge deflects the primary ion beam and accelerates the secondary ions in an undetermined manner. A simple but effective solution to this problem is to compensate this charge with an intense electron beam. Without charge compensation, no signal could have been obtained for the SBN samples analyzed in this study. Therefore, charge compensation was used for all the measurements we made during this study.

2.2 Depth Profiling

The three SBN samples were doped with Cr at nominal values of 0.005, 0.025, and 0.010 wt.%. For each sample at least three depth-profiling measurements were taken from different spots (A, B, and C). The primary oxygen ion beam energy was 6 keV with ~200 nA current on the sample surface. Since these samples were excellent insulators, it was not possible to collect any secondary ion signal because of the charging effect on the sample surface. When we bombarded the sample with a 1-keV electron beam of 2.7 A (filament), we then were able to obtain a measurable secondary ion signal. It would have been impossible to obtain the data without an electron gun.

3. Results and Discussion

3.1 Presence of Cr

With electron beam bombardment, we were able to obtain chromium and the major substrate constituents (Sr, Ba, Nb) ion signals from all three samples. For each depth profile, we took 50 layers of data points. Among the chromium isotopes, mass number 52 was chosen because Cr 52 is most abundant and there is no possibility of mass interference with other secondary ions.

We selected Sr counts as a benchmark. The average signal counts of Cr dopant were then normalized against Sr counts from the A spot of the 0.005 wt.% Cr-doped sample. As the data in table 1 show, these values are not proportional to the nominal values. One disadvantage of SIMS analysis is that it is not possible to get quantitative numbers unless standard samples with known dopant concentrations are available. It appears that the samples were either mislabeled or the gravimetric dopant quantity was incorrect.

3.2 Uniformity

To determine the uniformity of Cr dopant throughout the sample, at least three different spots (A, B, and C) were chosen from which to obtain depth-profile measurements. A difficulty was associated with the readjustment of the SIMS instrument whenever the measuring spot was changed. To make a reliable comparison, we needed a benchmark. For this reason, we included ions of three major constituents (Sr, Ba, Nb) as well as Cr counts for depth profiling. In each case, we normalized Cr counts against Sr counts for the A spot of the 0.005 wt.% sample, since the composition of the major constituents was identical for all the samples. Comparing the three graphs in figure 2, we note that the beginning of the 0.010 wt.% data points is different from the other two graphs. At the start of data collection for the SIMS measurement, there is an idiosyncrasy we must take into account, i.e., that the first few data points are always unstable. For this reason, the first few data points for figures 2(b) and (c) were not collected.

Average values were obtained from the compiled data. All the values were normalized against the 0.005 wt.% spot A Cr counts using Sr counts as a benchmark. From table 2, we conclude that there are variations in the uniformity of Cr dopant concentration throughout the surface and that the contents are not proportional as expected.

Table 1. Average and normalized counts for three nominally doped Cr samples.

Sample	Average counts	Normalized counts
0.005% Cr	50	50
0.010% Cr	70	32
0.025% Cr	150	114

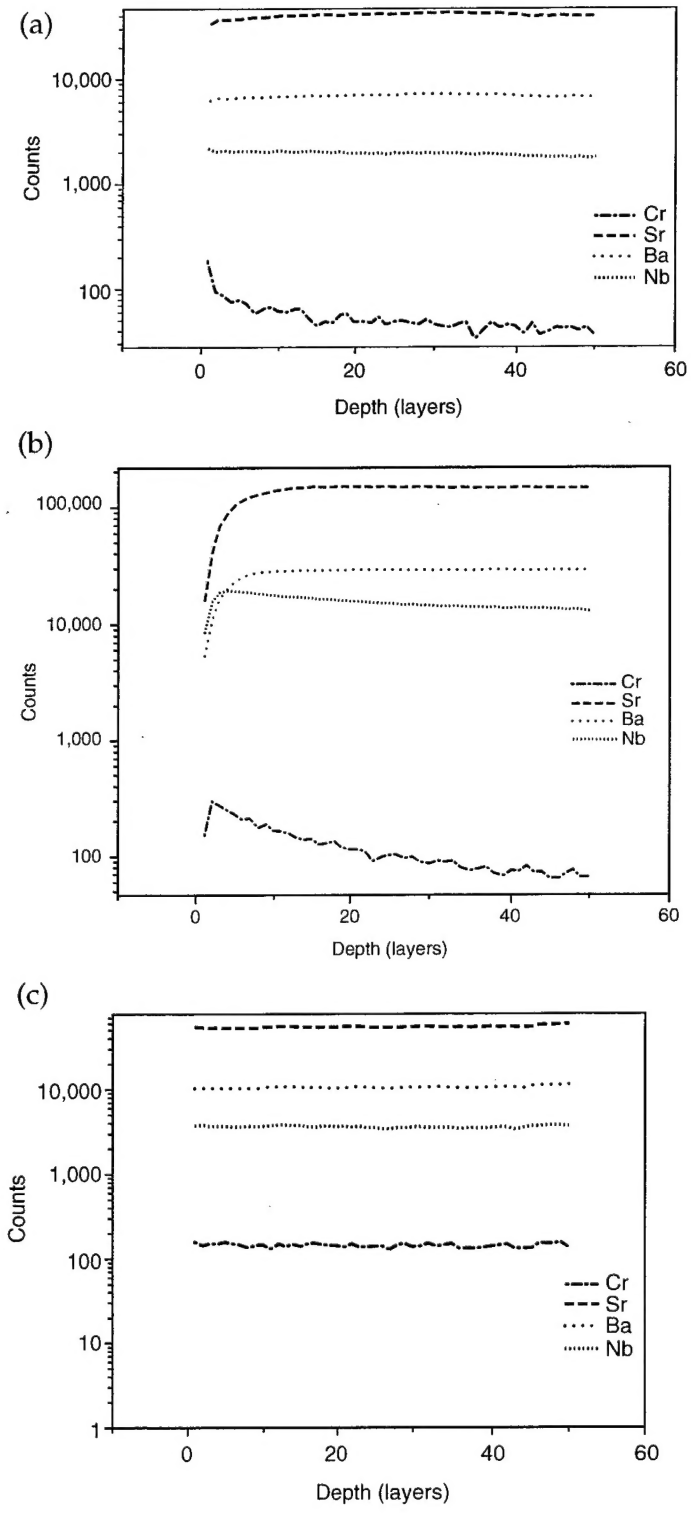

Figure 2. SIMS data for nominal value samples of (a) 0.005%, (b) 0.010%, and (c) 0.025% Cr.

Table 2. Counts for spots A, B, and C for three nominally doped Cr samples.

	Cr counts		
Sample	Spot A	Spot B	Spot C
0.005%	50	30	30
0.010%	32	21	21
0.025%	114	105	210

4. Summary

First, we confirmed that Cr dopants had been incorporated into the SBN samples during the crystal growth process, a finding that was not possible using any other technique to date. We cannot say that the dopant proportionality is close to the proposed values. To calculate the absolute quantity of Cr dopant incorporated into the samples, we need standard samples that have exactly the same SBN matrix with a known quantity of dopants.

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